

## METASTABILITY OF ISOFORMYL IONS IN COLLISIONS WITH HELIUM AND HYDROGEN

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## ABSTRACT

The stability of  $\text{HOC}^+$  ions under conditions in interstellar molecular clouds is considered. In particular the possibility that collisions with helium or hydrogen will induce isomerization to the stable  $\text{HCO}^+$  form is examined theoretically. Portions of the electronic potential energy surfaces for interaction with He and H atoms are obtained from standard quantum mechanical calculations. Collisions with He atoms are found to be totally ineffective for inducing isomerization. Collisions with H atoms are found to be ineffective at low interstellar temperatures owing to a small (about 500 K) barrier in the entrance channel; at higher temperatures where this barrier can be overcome, however, collisions with hydrogen atoms do result in conversion to the stable  $\text{HCO}^+$  form. Although detailed calculations are not presented, it is argued that low-energy collisions with  $\text{H}_2$  molecules are also ineffective in destroying the metastable ion.

*Subject headings:* molecular processes

## I. INTRODUCTION

The metastable isoformyl ion  $\text{HOC}^+$  is similar in many respects to its isoelectronic analog isocyanide,  $\text{HNC}$ . The latter species was first identified in the gas phase on the basis of interstellar microwave observations of its fundamental  $J = 1-0$  rotational transition, and this was confirmed by subsequent laboratory observations. Although lying about  $61 \text{ kJ mol}^{-1}$  above the stable  $\text{HCN}$  isomer, the barrier against unimolecular rearrangement is predicted to be on the order of  $140 \text{ kJ mol}^{-1}$ . The two isomers are found to have comparable abundances in interstellar clouds. The formyl ion,  $\text{HCO}^+$ , was also first observed spectroscopically in interstellar space and then confirmed in laboratory studies (see, e.g., Green 1981). Recently the microwave spectrum of  $\text{HOC}^+$  has been obtained in the laboratory (Gudeman and Woods 1982; Blake *et al.* 1983). Subsequent searches in interstellar space (Woods *et al.* 1983) provided a possible detection of the  $J = 1-0$  rotational transition in one source; however, observations of other transitions will be needed to confirm this identification. The most striking result, however, was the finding that  $\text{HOC}^+$  is at least two orders of magnitude less abundant than  $\text{HCO}^+$  in the 14 sources examined.

The abundances of molecules in interstellar space depend on the rates of creation and destruction. In most models of interstellar chemistry  $\text{HCO}^+$  is formed mainly by proton transfer from  $\text{H}_3^+$  to CO. It was suggested some time ago by Herbst *et al.* (1976), based on theoretical arguments, that this reaction might lead to roughly equal amounts of  $\text{HCO}^+$  and  $\text{HOC}^+$ . In that case (as discussed by Woods *et al.* 1983) the models predict an  $\text{HOC}^+:\text{HCO}^+$  ratio much higher than the upper limit set by observations. Very recently experimental evidence, albeit indirect, has been obtained by Illies, Jarrold, and Bowers (1982) which suggests that  $\text{HOC}^+$  is only a minor product ( $\approx 1\%-10\%$ ) in proton transfer from  $\text{H}_3^+$  to CO. Even with this smaller rate for creation, however, the models appear to predict more  $\text{HOC}^+$  than is observed (Blake *et al.*

1983). This suggests the existence of a mechanism to destroy  $\text{HOC}^+$  beyond those included in the standard chemistry models.

Woods *et al.* (1983) hypothesize that  $\text{HOC}^+$  reacts only very slowly with the dominant species in interstellar molecular clouds,  $\text{H}_2$  and He; they assume that the main reaction with the former will be radiative association. On the other hand, they suggest that H atoms will rapidly catalyze isomerization of  $\text{HOC}^+$  to  $\text{HCO}^+$ , and they interpret the low observed abundance of the metastable as evidence for a much larger fraction of H atoms than is generally thought to exist in these regions.

The purpose of this paper is to reconsider the metastability of  $\text{HOC}^+$  in collisions with hydrogen and helium. A neutral closed-shell species such as  $\text{HNC}$  is expected to interact only weakly with  $\text{H}_2$ , He, or H, forming van der Waals complexes in which the separate species are only slightly perturbed; the large abundance of  $\text{HNC}$  in interstellar space confirms that thermal collisions with  $\text{H}_2$  and He do not effect isomerization to the more stable  $\text{HCN}$ . An ion, like  $\text{HOC}^+$ , on the other hand, interacts via stronger, longer ranged, ion induced dipole forces. Owing to such forces, as is well known, ion molecule reactions generally have much larger rate constants than neutral reactions, and exothermic ion molecule reactions often have no activation barrier and proceed at every collision. To determine whether these forces can induce isomerization in thermal collisions, of course, requires a detailed study of the potential energy surfaces involved.

In order for a reaction to proceed at the low temperatures in dense interstellar molecular clouds, there must be no energy barriers between reactants and products; i.e., there must be a reaction path along which the potential energy never rises above that of the initial species. The present work uses standard ab initio molecular orbital methods to calculate the electronic potential as a function of the nuclear coordinates and to search for energetically allowed reaction paths. A difficulty in such a study is the large number of nuclear degrees of freedom that must be considered even for a four atom system such as  $\text{H-HOC}^+$  or  $\text{He-HOC}^+$ , but this is alleviated

<sup>1</sup>  $1 \text{ kJ mol}^{-1} = 0.239 \text{ kcal mol}^{-1} = 0.0104 \text{ eV}$ .

to some extent by using the gradient of the potential to help locate stationary points—local minima and transition states.

Calculations have been done for He and H atoms colliding with  $\text{HOC}^+$ , and details are given in the next two sections. He atoms are found to be entirely ineffective for causing isomerization. It is also concluded that H atoms probably do not induce isomerization in low energy collisions owing to a small but significant activation barrier in the entrance channel; if this barrier (about 500–1000 K) can be overcome, however, H atom collisions do lead to isomerization. Analogous calculations for  $\text{H}_2$  collisions are more difficult for two reasons: first, the additional atom increases the amount of coordinate space that must be examined, and, second, some of the important portions of this surface—unlike in the He and H atom cases—probably are not adequately described by molecular orbital (Hartree-Fock) wave functions, but require more sophisticated calculations. Nevertheless, it will be argued in § IV that isomerization in  $\text{H}_2$  collisions is also unlikely since one expects significant activation barriers in the entrance channel. In the absence of a fast destruction mechanism the low observed interstellar abundance of  $\text{HOC}^+$  suggests that, contrary to earlier suggestions, proton transfer from  $\text{H}_3^+$  to CO produces very little of the metastable isomer.

## II. He COLLISIONS

Although He atoms are generally considered to be inert, they can form moderately strong bonds in ionic species such as  $\text{HeH}^+$  and  $\text{HeCN}^+$  (Wilson and Green 1980). Note that the latter is isoelectronic with HCN and has an analogous structure, but there are significant differences in their bonding. It seems plausible that He might facilitate isomerization of  $\text{HOC}^+$  by a chaperone mechanism: He attacks the proton, forming a partial He-H bond, and this weakens the H-O bond, lowering the barrier to rotation about CO. It is also possible to imagine a rearrangement that proceeds through a  $\text{HeHCO}^+$  complex analogous to the isoelectronic formaldehyde structure.

To examine these possibilities, portions of the electronic potential energy surface were obtained from Hartree-Fock calculations. These employed a standard “split-valence”

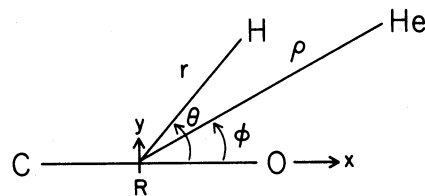


FIG. 1.—Coordinate system used to study chaperone mechanism for isomerization of  $\text{HOC}^+$  in collisions with He atoms.

(4–31 G) basis set on the C, O, and H nuclei which includes one contracted Gaussian orbital for the inactive 1s core orbitals of carbon and oxygen and two contracted Gaussian orbitals for the valence 2s and 2p orbitals and also for the hydrogen 1s orbital. On He a standard “double-zeta” basis was used, i.e., two contracted Gaussians for the 1s orbital; a 2p polarization function was also included on He to help describe the expected ionic nature of the bonding. Some calculations that included additional C3d, O3d, and H2p polarization functions indicated that these did not make any qualitative changes. Experience with analogous calculations on  $\text{HeH}^+$  and  $\text{HeCN}^+$ , including comparison with experiment for the former, suggests that calculations at this level of approximation give an adequate description of the electronic structure (see also Farnell, Pople, and Radom 1983).

Efforts to locate a stable (or metastable) formaldehyde-like  $\text{HeHCO}^+$  structure were unsuccessful. Only very high energy states that directly dissociated were obtained, and these will not play any role in collision-induced isomerizations.

To examine the possibility of a chaperone mechanism a series of calculations were done to obtain the electronic energy along the  $\text{HOC}^+ \text{--} \text{HCO}^+$  path, defined by the angle,  $\theta$ , of the proton about the midpoint of the CO bond (see Fig. 1). Thus  $\theta = 0^\circ$  corresponds to the isoformyl ion and  $\theta = 180^\circ$  corresponds to the stable structure. For a set of angles the CO distance,  $R$ , and the distance from the CO midpoint to H,  $r$ , were optimized using analytic gradients and standard numerical techniques (McIver and Komornicki 1971) to find the lowest energy for the fixed angle. The structure was then reoptimized in the presence of a He atom. Results, which are summarized in Table 1, indicate that He forms only a very

TABLE 1  
INFLUENCE OF He ON ISOMERIZATION OF  $\text{HOC}^+$  <sup>a</sup>

$\theta$	$\text{HCO}^+$			$\text{HCO}^+ \text{--} \text{He}$				
	$E$ , kJ mol <sup>−1</sup> <sup>b</sup>	$R/a_0$	$r/a_0$	$\Delta E$ , kJ mol <sup>−1</sup> <sup>b,c</sup>	$\Delta R/a_0$	$\Delta r/a_0$	$\rho/a_0$	$\phi$
0°	91.0	2.193	2.941	−3.6	−0.002	+0.005	6.175	0°
30°	122.0	2.220	2.760	−3.3	−0.002	+0.003	6.012	38.4°
60°	254.7	2.234	2.389	...	...	...	...	...
90°	406.3	2.174	2.353	−3.3	−0.003	+0.033	5.467	87.5°
120°	308.8	2.101	2.673	...	...	...	...	...
150°	90.4	2.080	2.929	−1.3	0.000	+0.001	6.705	132.0°
180°	0.0 <sup>b</sup>	2.075	3.075	−1.6	0.000	+0.001	7.036	180.0°

<sup>a</sup> Obtained from Hartree-Fock calculations as described in the text; the coordinate system is shown in Fig. 1.

<sup>b</sup> Energies are given relative to  $\text{HCO}^+$  at equilibrium and He at infinity, the total energies of which are calculated to be −112.7793 hartree and −2.8612 hartree, respectively. 1 kJ mol<sup>−1</sup> = 0.239 kcal mol<sup>−1</sup> = 0.0104 eV. Distances are in bohr radii, 1a<sub>0</sub> = 0.5292 × 10<sup>−8</sup> cm.

<sup>c</sup>  $\Delta E$  is the binding energy, i.e., the energy change on bringing the He atom from infinity to the minimum energy configuration (for fixed  $\theta$ ).

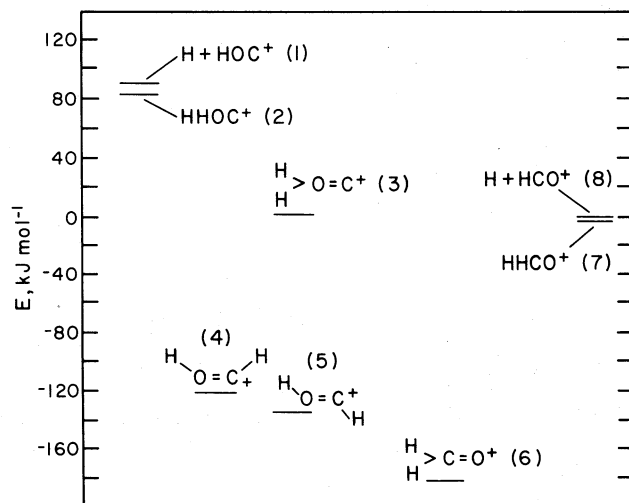


FIG. 2.—Relative energy of metastable points on the potential energy surface of a hydrogen atom interacting with an  $\text{HCO}^+$  ion. Parenthetical numbers correspond to those in Table 2 and in the text.

weak complex with the ion. It is clear that collisions with He are totally ineffective in promoting isomerization. The binding found in the complex is consistent with a simple electrostatic model. The ion induces a dipole in He, and this interacts with the charge to give a long-range isotropic attraction. The permanent dipole of the ion also interacts with the induced dipole, causing the He to be oriented toward the proton.

The isomerization of isolated  $\text{HOC}^+$  has recently been studied theoretically in some detail by Nobes and Radom (1981). Their results at the same level of theory as used here (HF/4-31 G) are essentially the same; however, they have also considered more extensive calculations finding that adding polarization functions to the basis set significantly decreases the barrier and increases the isomerization energy and that adding correlation effects gives somewhat smaller changes in the same direction.

### III. H ATOM COLLISIONS

Several mechanisms can be envisioned in which collision of a hydrogen atom with  $\text{HOC}^+$  leads to isomerization to  $\text{HCO}^+$ .

A chaperone mechanism like that considered in He collisions is plausible. Also  $\text{H}_2\text{CO}^+$  is known to have several metastable isomers that might serve as intermediates along a reaction path, including cases where the attaching H atom becomes incorporated in the product, displacing the original hydrogen. Figure 2 indicates schematically the energy of relevant stable points on the  $\text{H}_2\text{CO}^+$  surface. Properties of these species, calculated with the unrestricted Hartree-Fock approximation and the 4-31 G Gaussian basis (UHF/4-31 G), are given in Table 2. Calculations on some of these have been reported previously by Bouma, MacLeod, and Radom (1980) and by Osamura *et al.* (1981). The earlier results are in good accord with the present study. They also demonstrate that use of a spin-restricted HF formalism, as opposed to the unrestricted HF formalism used here does not cause any significant changes, and that inclusion of polarization basis functions or configuration interaction does not qualitatively alter any of the present conclusions. It is seen that addition of a hydrogen atom to  $\text{HOC}^+$  is energetically possible at both the oxygen end, to form  $\text{H}_2\text{OC}^+$  (3) or at the carbon end to form *cis*- $\text{HCOH}^+$  (4) or *trans*- $\text{HCOH}^+$  (5). Enough energy is available from these additions that 1, 2 hydrogen shifts must be considered; i.e., rearrangements from (3) to (4) or (5) and from (4) or (5) to (6) might be accessible. Finally, removal of a hydrogen from the oxygen end of (4) or (5) or from the carbon end of (6) is seen to be energetically feasible and to yield the stable  $\text{HCO}^+$  isomer.

Whether isomerization can actually occur along any of these paths depends on whether or not there are insurmountable barriers (i.e., potential energies higher than the reactants) on the surface between reactants and products. To examine this point calculations have been done for several relevant portions of the surface at the UHF/4-31 G level of theory. As with the He calculations, an internal reaction coordinate is chosen that can be varied smoothly on going from one configuration to another; and, for fixed values of this coordinate, the other coordinates are varied to minimize the energy.

Some care needs to be exercised in choosing an appropriate internal reaction coordinate to vary. As an example, in examining the addition of hydrogen to the oxygen end of  $\text{HOC}^+$ , i.e., the path from (1) to (3) in Figure 2, the reaction

TABLE 2  
CALCULATED PROPERTIES OF METASTABLE  $\text{H}_2\text{CO}^+$  STRUCTURES<sup>a</sup>

Species	Energy, $\text{kJ mol}^{-1}$	Structure	Vibrational Frequencies, $\text{cm}^{-1}$
(1) $\text{H} + \text{HOC}^+$ .....	91.0	$R(\text{CO}) = 2.193, R(\text{OH}) = 1.844$	505, 505, 2003, 3599
(2) $\text{HHOC}^+$ .....	82.7	$R(\text{CO}) = 2.190, R(\text{OH}) = 1.864, R(\text{HH}) = 3.516$	151, 151, 364, 617, 617, 2012, 3377
(3) $\text{COH}_2^+$ .....	2.0	$R(\text{CO}) = 2.799, R(\text{OH}) = 1.835$ $\angle \text{COH} = 122^\circ$	739, 855, 988, 1828, 3682, 3792
(4) <i>cis</i> - $\text{HCOH}^+$ .....	-121.3	$R(\text{CO}) = 2.302, R(\text{OH}) = 1.840, R(\text{CH}) = 2.042$ $\angle \text{HCO} = 134^\circ, \angle \text{COH} = 131^\circ$	986, 998, 1178, 1788, 3298, 3647
(5) <i>trans</i> - $\text{HCOH}^+$ .....	-136.3	$R(\text{CO}) = 2.311, R(\text{OH}) = 1.838, R(\text{CH}) = 2.041$ $\angle \text{HCO} = 126^\circ, \angle \text{COH} = 128^\circ$	1006, 1032, 1276, 1762, 3328, 3683
(6) $\text{H}_2\text{CO}^+$ .....	-183.2	$R(\text{CO}) = 2.328, R(\text{CH}) = 2.046$ $\angle \text{HCO} = 118^\circ$	1110, 1289, 1477, 1645, 3199, 3342
(7) $\text{HHCO}^+$ .....	-4.1	$R(\text{CO}) = 2.075, R(\text{HC}) = 2.048, R(\text{HH}) = 3.846$	137, 137, 332, 1063, 1063, 2376, 3370
(8) $\text{H} + \text{HCO}^+$ .....	0.	$R(\text{CO}) = 2.075, R(\text{HC}) = 2.038$	1030, 1030, 2384, 3406

<sup>a</sup> From Hartree-Fock/4-31 G calculations. All structures are planar (or linear). Distances are in bohr radii.



TABLE 3

REACTION PATH FOR CHAPERONE MECHANISM WITH H ATOMS<sup>a</sup>

$\theta$	$R/a_0$	$r/a_0$	$\rho/a_0$	$\phi$	Energy, kJ mol <sup>-1</sup> <sup>b</sup>
0°	2.190	2.962	6.391	0.1°	82.7
5°	2.191	2.956	6.386	6.6°	83.3
15°	2.197	2.915	6.308	19.5°	88.9
30°	2.215	2.786	6.068	37.6°	112.8
60°	2.216	2.562	5.150	63.6°	238.9

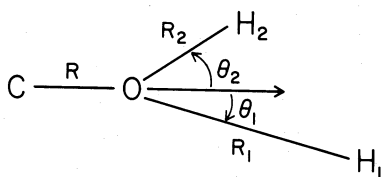
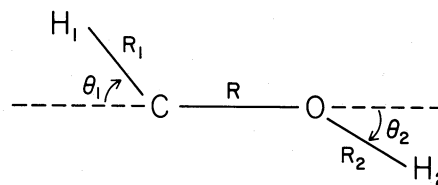
<sup>a</sup> Coordinate system as in Fig. 1.<sup>b</sup> Zero of energy is separated  $\text{HCO}^+ + \text{H}$  as in Table 2.

coordinate was initially chosen as the distance of one of the hydrogens to the CO midpoint. Calculations that started at the equilibrium structure, (3), however, did not head toward the desired product, (1), when the reaction coordinate was increased. Rather, they headed toward a  $\text{C}^+$  ion separating from a water-like  $\text{H}_2\text{O}$  fragment. Choosing the internal reaction coordinate alternately as one of the HO distances, on the other hand, gave a smooth dissociation in the desired manner.

The first reaction path considered is for the chaperone mechanism. The coordinates depicted in Figure 1 with the He atom replaced by a second hydrogen are appropriate here. The isomerization corresponds to variation of  $\theta$  from 0° to 180°. Relevant results for the beginning of this path are given in Table 3, from which it appears that interaction with a hydrogen atom is quite similar to interaction with He: the complex is only slightly bound, the incoming atom is aligned by the dipole charge-induced dipole interaction, and the barrier to isomerization is not significantly lowered.

The next mechanism to be considered is attack of the incoming hydrogen atom at oxygen to form the metastable isomer, (3). The coordinates used to describe this case are shown in Figure 3. The reaction coordinate is chosen as  $R_1$ , the distance from oxygen to one of the hydrogen atoms. From a computational standpoint it is most convenient to start at the equilibrium structure for (3) and increase  $R_1$ ; initial values for optimization of the other internal coordinates can then be taken from the previous calculation. Results are given in Table 4. It is seen that, although there is initially a long-range attraction as the hydrogen atom approaches the ion, reaching the linear metastable structure, (2), a very large barrier must be overcome to rearrange the complex to the  $\text{H}_2\text{OC}^+$  configuration, (3). This barrier precludes collision-induced isomerization along this path.

The third mechanism to be considered is attack of the incoming hydrogen atom at carbon. The coordinate system used here is shown in Figure 4; the reaction coordinate is  $R_1$ , the distance from one of the hydrogens to carbon.

FIG. 3.—Coordinate system used to study addition of a hydrogen atom to the oxygen atom in  $\text{HOC}^+$ .FIG. 4.—Coordinate system used to describe cleavage of the CH and OH bonds in  $\text{HCOH}^+$ .

above, calculations were started at the metastable structure, (5), and proceeded toward dissociation. Results are in Table 5. It is seen in this case that the initial approach of the hydrogen atom to the ion is slightly repulsive; a small, but probably significant barrier, equal to an energy of about 500 K, must be overcome before the complex can be formed. Because this path will prove to be the most favorable for reaction, it is important to consider whether the computed barrier is accurate. Note that the barrier occurs when the attacking hydrogen atom is still quite far away from the ion and with little distortion of the ion from its equilibrium structure. This suggests that the barrier arises from long-range electrostatic forces, and, in fact, a closer examination supports this. As for the case of He collisions, the dominant long-range term is interaction of the charge with the induced dipole, and this is always attractive, isotropic, and varies as  $R^{-4}$  for large  $R$ . The  $\text{HOC}^+$  ion has a sizable dipole, which also interacts with the induced dipole; this interaction varies as  $R^{-5} \cos \theta$ , being attractive at the positive end of the dipole and repulsive for the opposite orientation. Thus, there is a strong orientational preference for the incoming atom to approach the proton (positive dipole) end of the ion. Using appropriate values for the  $\text{HOC}^+$  dipole moment and the hydrogen atom polarizability, one finds that for intermediate distances,  $R = 3-4 a_0$ , the  $R^{-5}$  term overtakes the  $R^{-4}$  term, and the interaction is repulsive for approach along the carbon side. The HF approximation properly describes long-range electrostatic forces, and it is not surprising that the calculated barrier agrees well, in magnitude and orientation dependence, with this simple multipole estimate. Electron correlation effects that are ignored in the HF approximation are not expected to be important for long-range forces. Limited basis sets, especially lack of polarization functions, on the other hand, might lead

TABLE 4

REACTION PATH FROM  $\text{HOC}^+ + \text{H}$  TO  $\text{H}_2\text{OC}^+$  <sup>a</sup>

$R_1/a_0$	$\theta_1$	$R_2/a_0$	$\theta_2$	$R/a_0$	$E$ , kJ mol <sup>-1</sup> <sup>b</sup>
1.835	58.0°	1.835	58.0°	2.799	2.0
2.0	57.6°	1.836	57.8°	2.777	16.7
2.25	57.2°	1.836	57.5°	2.736	72.3
2.5	56.7°	1.837	57.2°	2.689	142.1
2.75	56.3°	1.838	55.9°	2.613	210.2
3.0	57.4°	1.853	32.1°	2.228	210.5
3.5	60.9°	1.846	20.1°	2.204	152.0
4.0	61.2°	1.844	10.0°	2.195	119.2
5.0	0.0°	1.873	0.1°	2.190	83.4
5.380	0.0°	1.864	0.0°	2.190	82.7
$\infty$	...	1.844	0.0°	2.193	91.0

<sup>a</sup> See Fig. 3 for coordinate system.<sup>b</sup> Separated  $\text{HCO}^+ + \text{H}$  is zero of energy as in Table 2.

TABLE 5  
REACTION PATH FOR CLEAVAGE OF CH BOND IN TRANS-HCOH<sup>+</sup> <sup>a</sup>

$R_1/a_0$	$\theta_1$	$R_2/a_0$	$\theta_2$	$R/a_0$	$E, \text{kJ mol}^{-1} \text{ }^b$
2.038	53.4°	1.838	52.3°	2.310	-136.3
2.25	54.4°	1.838	52.2°	2.311	-118.2
2.5	55.7°	1.838	51.4°	2.309	-68.8
2.75	57.8°	1.840	50.6°	2.305	-10.1
3.25	64.1°	1.841	40.6°	2.269	77.6
3.5	65.8°	1.838	24.3°	2.235	95.0
3.75	65.8°	1.837	-1.4°	2.212	99.0
4.0	67.6°	1.839	-0.2°	2.206	98.8
4.5	70.5°	1.842	-0.3°	2.198	95.2
$\infty$	...	1.844	0.0°	2.193	91.0

<sup>a</sup> See Fig. 4 for coordinate system.

<sup>b</sup> Zero of energy is separated HCO<sup>+</sup> + H as in Table 2.

to errors. Accordingly parts of the surface around this barrier were recalculated including polarization functions, with the conclusion that the UHF/4-31 G calculation provides a good estimate but that the actual barrier is probably about 50% higher.

Whether or not this barrier can be overcome in low temperature thermal collisions will be considered in some detail below. Assuming that it is, however, it is still necessary to consider the rest of the path to isomerization. This can occur most simply by cleavage of the OH bond in HCOH<sup>+</sup> (5). It can also occur via the less direct route of a 1,2 hydrogen shift that converts (5) to the stable H<sub>2</sub>CO<sup>+</sup> ion, (6), followed by cleavage of one of the HC bonds. This latter isomerization from (5) to (6) has been studied previously (Osamura *et al.* 1981) including the effect of basis set size and configuration interaction on the exoergicity and barrier height.

Cleavage of the OH bond was examined using the coordinate system in Figure 4;  $R_2$  is taken as the reaction coordinate here. Results of the UHF/4-31 G calculations are summarized in Table 6. It is seen that there is a sizable barrier (about 80 kJ mol<sup>-1</sup> above the asymptote) involved. However, this is less than the reaction exoergicity, and will not, therefore, impede isomerization by this mechanism. Unlike the barrier against cleavage of the CH bond in HCOH<sup>+</sup>, which owes to long-range forces, the barrier against OH bond cleavage results from a reorganization of the electronic structure that is involved. As discussed below, in that case the

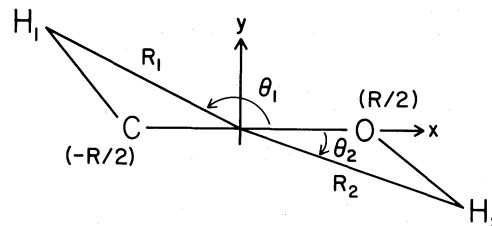


FIG. 5.—Coordinate system used to study isomerization of H<sub>2</sub>CO<sup>+</sup> to HCOH<sup>+</sup>.

addition of polarization functions and configuration interaction are likely to reduce the barrier further. It appears then that if a hydrogen atom colliding with HOC<sup>+</sup> can overcome the small barrier to formation of HCOH<sup>+</sup>, it can lead to isomerization to the stable HCO<sup>+</sup> via this mechanism.

The last path considered here is 1,2 hydrogen shift that converts trans-HCOH<sup>+</sup>, (5), to H<sub>2</sub>CO<sup>+</sup>, (6). The coordinates used for this case are shown in Figure 5. It is convenient to measure the distances to the hydrogens,  $R_1$  and  $R_2$ , from the midpoint of the CO bond, and to take the reaction coordinate as the angle,  $\theta_2$ . Results of UHF/4-31 G calculations are given in Table 7. A large barrier to 1,2 hydrogen shift is found; at this level of theory the predicted barrier is too high to be overcome by the exoergicity of the initial H + COH<sup>+</sup> step. It should be noted that Osamura *et al.* (1981) have considered the effect on this 1,2 shift of including polarization functions and configuration interaction in the wave function. As is often (although not always) the case, the more sophisticated treatment preferentially lowers the energy of contorted (less "classical") geometries, with the result that the barrier is substantially lowered. In fact, the lowering they find is enough to allow this rearrangement to proceed with the exothermicity calculated here for the hydrogen addition step. (To be consistent, of course, the exothermicity of hydrogen addition would have to be recalculated at the higher level of approximation.) For this mechanism to effect isomerization it is necessary finally that one of the hydrogens can be removed from H<sub>2</sub>CO<sup>+</sup> without an excessive barrier. This final segment of the surface has not been examined here because (1) there is likely to be only a small barrier, if

TABLE 7  
REACTION PATH FOR 1,2 HYDROGEN SHIFT<sup>a</sup>

$\theta_2$	$R_2/a_0$	$\theta_1$	$R_1/a_0$	$R$	$E, \text{kJ mol}^{-1} \text{ }^b$
0°	2.956	146.4°	2.896	2.274	-93.1
15°	2.897	145.0°	2.872	2.285	-111.6
30°	2.738	145.2°	2.877	2.306	-135.5
45°	2.522	146.5°	2.093	2.323	-113.4
60°	2.320	147.8°	2.926	2.326	-20.0
75°	2.195	148.8°	2.946	2.320	+107.2
90°	2.297	152.0°	2.981	2.298	+128.9
105°	2.418	152.1°	2.974	2.288	+4.2
120°	2.517	147.6°	2.914	2.313	-117.3
135°	2.718	141.9°	2.825	2.326	-179.1
150°	2.946	135.5°	2.722	2.326	-166.3
165°	3.127	128.6°	2.621	2.312	-84.5

<sup>a</sup> See Fig. 4 for coordinate system.

<sup>b</sup> Zero of energy is separated HCO<sup>+</sup> + H as in Table 2.

<sup>a</sup> See Fig. 5 for coordinate system.

<sup>b</sup> Zero energy is separated HCO<sup>+</sup> + H as in Table 2.

any, and (2) this mechanism provides a secondary path, the one discussed in the preceding paragraphs being sufficient.

The important question is then whether the small barrier to hydrogen addition to  $\text{HOC}^+$  will prevent formation of  $\text{HCOH}^+$  in low temperature thermal collisions. As discussed above, the calculated barrier height corresponds to a temperature of 500–1000 K and is not likely to be significantly in error. Classically, a hydrogen atom must have at least this much kinetic energy to react, and this would occur only in a tiny fraction of the atoms in the high energy tail of the Boltzmann distribution at interstellar temperatures. Two quantum mechanical effects might alter this picture. First, it is possible for hydrogen atoms to tunnel through the barrier, enhancing the low temperature rate. Because the barrier occurs at long range and the hydrogen has to tunnel a rather large distance, the tunneling rate will be fairly small at low energies. Working in the opposite direction is zero point vibrational motion that must be present in each bound degree of freedom; UHF/4–31 G calculations for the force constants at the transition state (top of the barrier) suggest that zero point motion will raise the effective height of the barrier by about 100 K. It appears on balance that at interstellar temperatures of less than 100 K, the rate of collision induced isomerization will be at least one to two orders of magnitude slower than the gas kinetic (Langevin) rate. Because hydrogen atoms are thought to have small fractional abundance in dense clouds, reaction with them is unlikely to represent an important loss mechanism for  $\text{HOC}^+$ . On the other hand, at laboratory or elevated temperatures, collision induced isomerization by hydrogen atoms can be important.

#### IV. $\text{H}_2$ COLLISIONS

Since  $\text{H}_2$  is the dominant component of the molecular gas, collisions of it with  $\text{HOC}^+$  are most important. Unfortunately, theoretical study of these is more difficult than the atomic case. First, the additional atom adds three dimensions to the coordinate space that must be examined. Second, some of the relevant parts of the surface are not expected to be adequately described at the single configuration (Hartree-Fock) level of theory; this is especially true for mechanisms that simultaneously break the  $\text{H}_2$  bond and form a bond to the ion. Although an extensive study of the relevant surface has not been done, preliminary calculations and qualitative arguments can be invoked to suggest that low energy collisions with  $\text{H}_2$  are not effective in isomerizing  $\text{HOC}^+$ .

As with He and H atom collisions, a chaperone mechanism for isomerization is plausible. Nobes and Radom (1981) have presented calculations for the weak complexes of  $\text{H}_2$  with both isomers of the ion, finding more stabilization for  $\text{H}_2\text{-HOC}^+$  than for  $\text{H}_2\text{-HCO}^+$ , as would be required for a chaperone mechanism to work. Preliminary calculations at the HF/4–31 G level of theory indicate that the barrier against isomerization is dramatically lowered in the complex—perhaps to less than a quarter of the value in the isolated ion—but that it is not

eliminated entirely. It appears that the remaining barrier of 30–40  $\text{kJ mol}^{-1}$  will preclude low energy collision-induced isomerization.

A second possibility is that reaction proceeds via  $\text{H}_2$  attack at the carbon end of  $\text{HOC}^+$  to form the stable  $\text{H}_2\text{COH}^+$  ion, with subsequent rearrangement and loss of hydrogen to form  $\text{HCO}^+$ . Preliminary calculations suggest that this mechanism, like the analogous H atom reaction, is hindered by repulsive long-range forces that preferentially orient the incoming  $\text{H}_2$  toward the proton end of the ion. Furthermore, experience with other systems suggests that there are likely to be large barriers in the entrance channel associated with breaking the  $\text{H}_2$  bond before the HC bonds can be formed. Similar barriers in the entrance channel are expected to preclude reaction via the other metastable intermediate,  $\text{H}_3\text{CO}^+$ . It thus appears that collisions with  $\text{H}_2$  are unlikely to destroy  $\text{HOC}^+$ . A more detailed analysis recently completed by DeFrees, McLean, and Herbst (1983) reaches the same conclusion.

#### V. CONCLUSIONS

It is found that  $\text{HOC}^+$  is stable in thermal collisions with He atoms, and it is argued that collisions with  $\text{H}_2$  molecules are likewise ineffective for inducing isomerization. Although these systems, like all ion molecule systems, have attractive long-range interactions, they have barriers in the entrance channel at closer range that preclude reaction. For collisions with H atoms, on the other hand, an isomerization reaction path has been located that has only a small barrier in the entrance channel. This path involves attachment of the incoming H atom at the carbon to give an  $\text{HCOH}^+$  ion, with subsequent cleavage of the OH bond. Although the barrier in the entrance channel is small, about 500–1000 K, it will significantly impede low temperature reactions. At interstellar temperatures of less than 100 K, the rate constant will probably be at least two orders of magnitude slower than the Langevin rate, suggesting that collisions with H atoms are *not* an effective means of destroying  $\text{HOC}^+$  in interstellar molecular clouds. It seems likely then that the low observed abundance of  $\text{HOC}^+$  in these objects reflects a creation rate that is smaller than has been assumed; in particular, it is likely that proton transfer from  $\text{H}_3^+$  to CO produces almost exclusively the stable isomer. Finally, it must be noted that, while the present study suggests the stability of  $\text{HOC}^+$  in collisions with  $\text{H}_2$ , further work to corroborate this point is warranted since even moderate destruction rates in collisions with  $\text{H}_2$  would also explain the low observed abundance of the metastable.

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